Thermochemical Data of Organic Ions Obtained from Investigations in the More or Less “Diluted” Gas Phase

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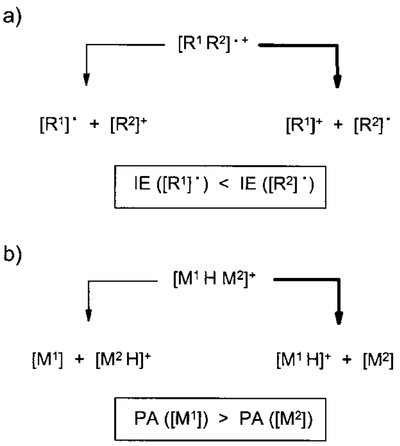
In memory of Bob Squires

The knowledge of quantitative thermochemical data for elementary steps of organic reactions falls short of the diversity of synthetic methods in organic chemistry. Whereas a qualitative assessment of relative stabilities, acidities, and basicities of starting materials and products supports our understanding of many reactions, it is only from heats of formation, enthalpies of deprotonation and protonation, electron affinities, and other thermochemical properties of the reactants and the reactive intermediates that we may achieve quantitative models of chemical reactions and a detailed understanding of chemical processes. Likewise, kinetic parameters for chemical conversions such as activation enthalpies are of central importance in this respect. In view of the multitude of solvents, catalysts, and reaction auxilaries that affect chemical reactions, efforts to attain a systematic order in this world are often misjudged because, even today, a new recipe can be developed much faster than can a comprehensive quantitative understanding of a chemical reaction. Nevertheless there is progress that may also support the (often neglected) pretention of chemistry to be both a discipline of science *and* culture.

This contribution highlights recent progress in the field of gas-phase chemistry, which has been achieved by measurements concerning the reactivity of organic ions in the “dense” (namely, more or less “diluted”) gas phase, that is, in the range of approximately 1–1500 mbar. It will demonstrate by discussing a highly impressive investigation in detail, and also some independent work, the ways in which we can bridge the gap between the chemistry of organic ions in the condensed phase that is the domain of synthetic chemists, on the one hand, and the chemistry of isolated, unsolvated ions in vacuo, on the other.

Soon after the first applications of mass spectrometry as a technique for analyzing volatile organic compounds it was discovered that the intrinsic properties of molecules, radicals, and ions in the diluted gas phase determine the unimolecular decomposition and thus the analytical information of these gaseous ions. For example, the Stevenson–Audier rule[1] states that the fragmentation of a radical cation $[R^1R^2]^{\bullet+}$ yields the cationic fragment whose corresponding neutral species, that is, the radical $[R^1]^\bullet$ or $[R^2]^\bullet$, or molecule $[M^1]$ or $[M^2]$, has the lower ionization energy (IE) (Scheme 1 a).[2] Cooks et al.[3] later developed a method to determine proton affinities (PA), by making use of the dissociation of a protonated adduct of two different molecules (a protonated “heterodimer”) $[M^1HM^2]^+$, to give the proton affinity of a molecule (M^1 or M^2) if that of the other molecule (M^2 or M^1, respectively) is known (Scheme 1 b).[4]



Scheme 1. Schematic representation of the priciples a) of the Stevenson–Audier rule and b) of the kinetic method.

The large variety of methods that allow us to study isolated ions in the high vacuum of mass spectrometers, namely in the “diluted gas phase” at 10^{-9}–10^{-5} mbar, has enabled large compilations of thermodynamic data on gaseous ions, molecules, and radicals to become available.[5] This world of data is growing steadily and is not limited to organic compounds, but will include inorganic, element-organic, and biochemical species to increasing extents.[6]

Quantitative data on Brønsted- and Lewis-acid catalyzed reactions are of particular importance.[7] Thus, complexation

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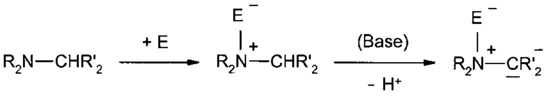
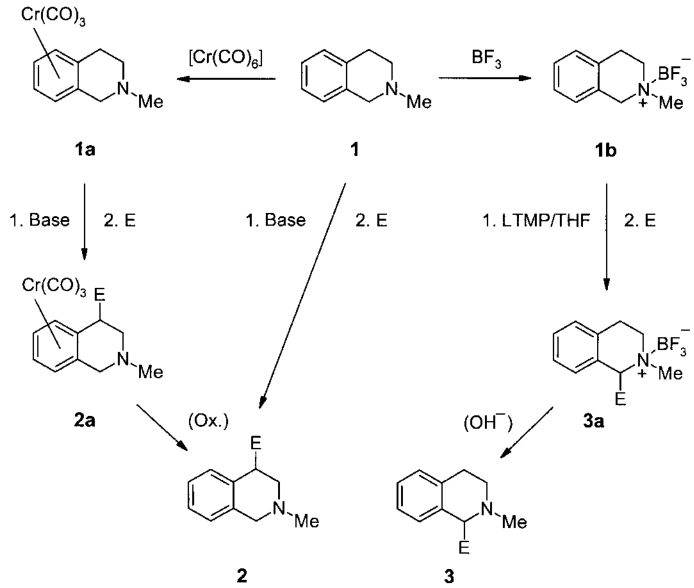
of carbonyl compounds by Lewis acids is well known to increase the electrophilicity of carbonyl groups, the acidity of adjacent C^{α}–H bonds, and the dienophilicity of the reactant. In contrast, activation of C^{α}–H bonds attached to *saturated* functional groups by Lewis acids is often much more difficult. Thus, useful synthetic methods for α-alkylations and α-acylations of tertiary amines have become available only recently.[8] These methods make use of the coordination of Lewis acids E to the nitrogen atom to increase the C^{α}–H acidity of the substrate [Eq. (1)].

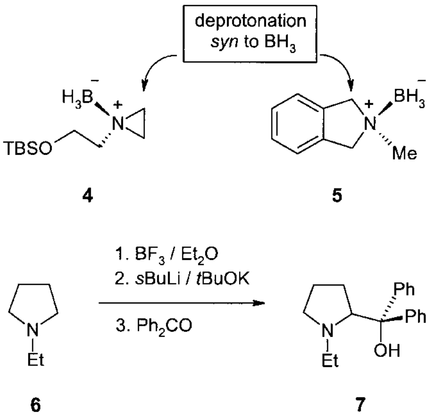


$$R_2N{-}CHR'_2 \xrightarrow{+E} R_2\overset{E^-}{\overset{|}{N^+}}{-}CHR'_2 \xrightarrow[-H^+]{(Base)} R_2\overset{E^-}{\overset{|}{N^+}}{-}\overset{-}{\underline{C}}R'_2 \qquad (1)$$

Some impressive and most recent examples are collected in Schemes 2 and 3. Whereas deprotonation of *N*-methyl-1,2,3,4-tetrahydroisoquinoline (**1**) and its $Cr(CO)_3$ complex **1a** with *n*-butyllithium occurs at C4 in the absence of Lewis acids,[9, 10] the formation of **1b** by complexation of **1** with boron trifluoride gives rise to deprotonation at C1.[11, 12] Instead of the complexes **2a** and the free bases **2**, the complexes **3a** are formed with high regioselectivity and they can be isolated readily and converted into the corresponding 1-alkylisoquinolines **3**. Recently, alkylation of Tröger's bases at the benzylic positions was considerably improved by using this method.[13] Borane has also been used in place of boron trifluoride.[11, 14–17] With this Lewis acid the 1-alkylation of **1** also takes place in very good yield, in analogy to the sequence **1**→**1b**→**3a**→**3**.[15]



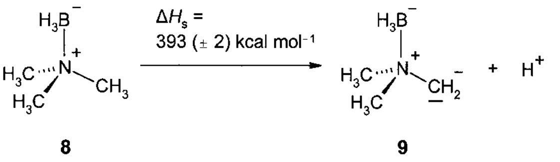
Scheme 2. Regioselective deprotonation of free and complexed **1**. LTMP = lithium 2,2,6,6-tetramethylpiperidide.



Scheme 3. Deprotection/alkylation of borane-complexed tertiary amines. TBS = *tert*-butyldimethylsilyl.

Another recent work demonstrates that this methodology can be successfully applied to the α-alkylation of *N*-alkylaziridines,[18] and it has been revealed that the incoming substituent preferentially attacks the complex **4** at the *syn* position relative to the BH_3 ligand (Scheme 3). This stereoselectivity was confirmed in the case of the *N*-methylisoindole–borane complex **5**. Moreover, use of *sec*-butyllithium/(−)-sparteine as an enantioselective deprotonation reagent led to remarkably high *ee* values for the alkylated complex.[17] With even stronger bases, such as those of the Lochmann–Schlosser type (for example, *s*BuLi/KO*t*Bu),[19] alicyclic amines such as *N*-ethylpyrrolidine (**6**) can be deprotonated and added to carbonyl compounds (Scheme 3).[20] Thus, in summary, deprotonation/alkylation of borane-complexed tertiary amines offers a considerable extension to the chemistry of dipole-stabilized carbanions that have been known for more than twenty years.[21–24]

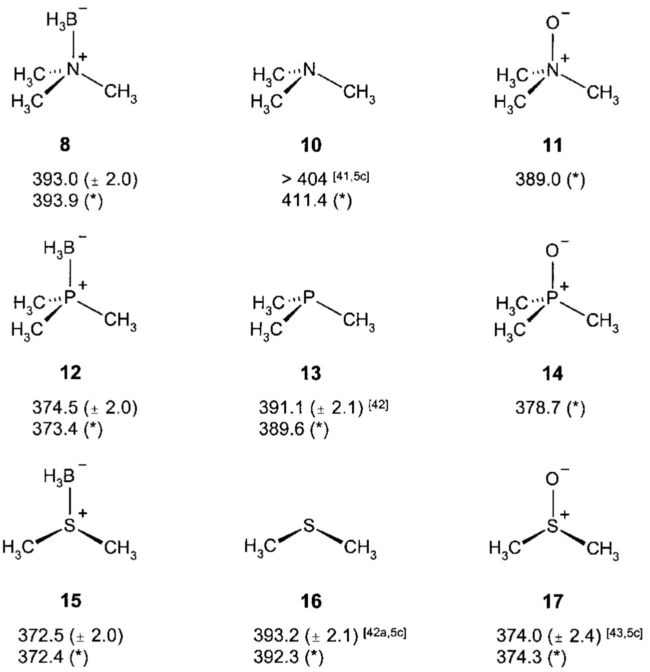
What can be gained now and added to this novel chemistry in solution from investigations in the diluted gas phase? The gas-phase C-H acidities of the volatile complexes of trimethylamine, trimethylphosphane, and dimethyl sulfide with BH_3 were studied in 1997 by Squires et al.[25] by employing flowing-afterglow mass spectrometry (FA-MS) or, more precisely, selected ion flow tube mass spectrometry (SIFT-MS).[26, 27] In this impressive work the authors demonstrated, for the first time and on a quantitative scale, the tremendous increase of the C-H acidity of aliphatic amines, phosphanes, and sulfides (**10**, **13**, and **16**, see Scheme 4) that is induced by the BH_3 ligand. In Equation (2) the prototypical dissociation



(2)

of the trimethylamine–borane complex **8** as a gaseous Brønsted acid is shown. The thermodynamic activation in this case, and in the corresponding adducts of BH_3 with trimethylphosphane (**12**) and dimethyl sulfide (**15**), were found to be as large as 18–21 kcal mol^{-1}; thus, the equilibrium constant of the dissociation of the C^{α}-H bond increases by $10^{13} < \Delta K_s < 10^{15}$, which is very similar to the acidifying effect from the oxygen atom in the related amine oxides, phosphane oxides, and sulfoxides (**11**, **14**, and **17**, respectively; Scheme 4).

A schematic diagram of contemporary[28] flowing-afterglow mass spectrometers based on the "selected ion flow tube" (SIFT) methodology is given in Figure 1. Ions generated in a flowing-afterglow ion source are selected according to their mass by a quadrupole mass filter (Q0) and introduced into a



Scheme 4. Brønsted acidities H_s (in kcal mol^{-1}) of the gaseous borane adducts **10**, **13**, and **16**, as compared to those of the free Lewis bases and the corresponding oxides. Unless quoted explicitely, the experimental and calculated (*) data were taken from Squires et al.[25]

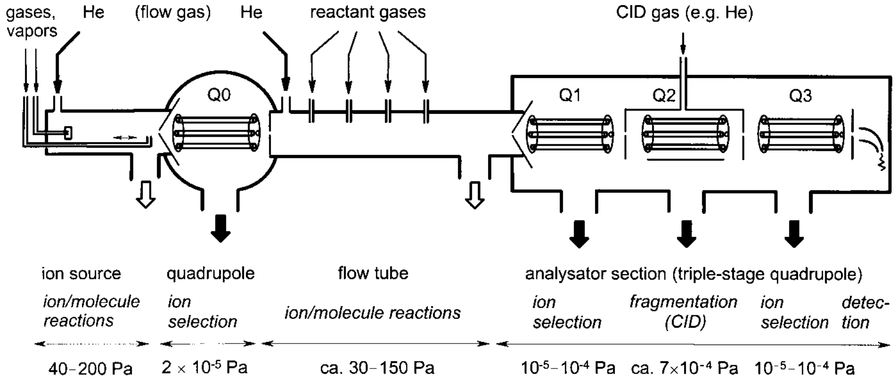
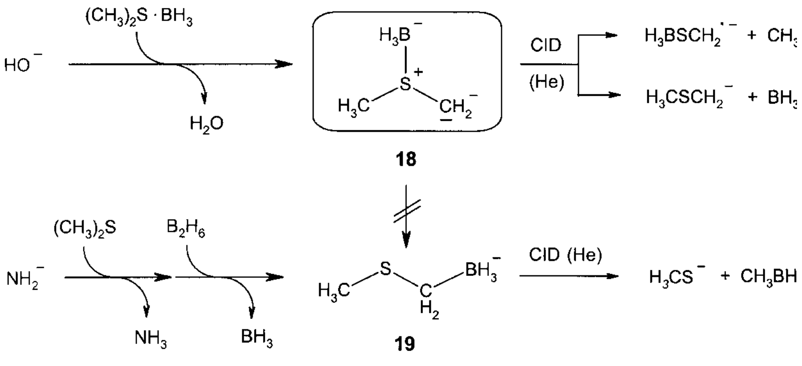


Figure 1. Schematic representation of a flowing-afterglow mass spectrometer. Selection of the reactant ions in the quadrupole mass filter (Q0) is followed by analysis of the product ions in a triple-stage quadrupole mass spectrometer (Q1/Q2/Q3).

reaction tube approximately 1 m in length, where they are allowed to migrate downstream in a flow of helium gas at a pressure of 0.3–1.4 mbar (ca. 30–140 Pa). Owing to the relatively high pressure in the flow tube these "reagent ions" are quickly cooled to the temperature of the carrier gas ("thermalized") by collisions with the helium atoms; therefore, they undergo ion/molecule reactions under thermal equilibrium with the volatile compounds injected into the gas stream through an inlet port. The product ions generated in this way can be subjected to characteristic ion/molecule reactions, such as proton transfer and H/D exchange reactions, by adding further gases "downstream" of the flow tube. At the end of the flow tube the carrier gas and other volatile neutrals are pumped off and the product ions are identified and characterized by means of a triple-stage quadrupole mass spectrometer (TSQ-MS); their relative abundances reflect the chemical equilibrium attained within the flow tube and, owing to the well-defined concentrations and flow parameters, they also yield kinetic information. To identify the product ions after being mass-selected in the first quadrupole filter (Q1), they are decomposed in a structure-specific manner in the zone of the second quadrupole (Q2) by collisions with inert gases, as eventually determined by mass analysis of the fragment ions in the third quadrupole (Q3).

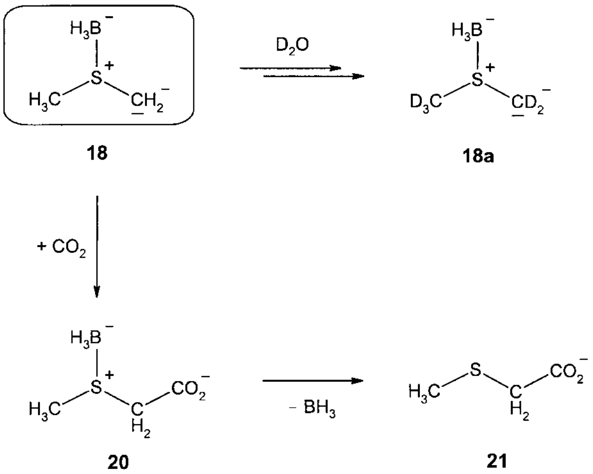
Squires et al. generated mass-selected OH^- ions and treated them with the volatile complexes **8**, **12**, and **15** in the flow tube. Organic anions generated by deprotonation [for example, **9** from **8**, Eq. (2)] were analyzed according to their mass and structure by collision-induced dissociation (CID) at the end of the flow tube after leaking into the triple-stage quadrupole mass spectrometer. The addition of reagent gases of known acidity into the flow tube allowed the authors to accurately determine the basicity of the anions generated within the flow tube by using the "bracketing" approach. The addition of suitable deuterated reagent gases, such as D_2O, revealed the number of exchangeable ("acidic") protons. Similar to the anions generated initially, the product anions of the subsequent reactions were mass-analyzed and structurally characterized by CID in the TSQ analyzer. In this way, Squires et al. found that the anion **9** formed from the trimethylamine–borane complex incorporates up to eight deuterium atoms. A detailed study on anion **18** generated from the dimethyl sulfide–borane complex **15** demonstrates the stringency of the method.

Mass-selected OH^- ions deprotonated the complex **15** in the flow tube to give $C_2H_8BS^-$ ions having the ylide structure **18**, and the collision-induced decomposition of **18** in the triple-stage quadrupole analyzer was found to be characteristically different from that of the isomeric ions **19**, which were generated by an independent reaction sequence involving NH_2^-, Me_2S, and B_2H_6 (Scheme 5). According to ab initio calculations the isomerization **18**→**19** is exothermic but kinetically suppressed by a high activation barrier (29 kcal mol^{-1}).[25b]



Scheme 5. Generation of isomeric anions $C_2H_8BS^-$ by ion/molecule reactions and characterization by collision-induced dissociation (CID) in the SIFT mass spectrometer (see Figure 1).

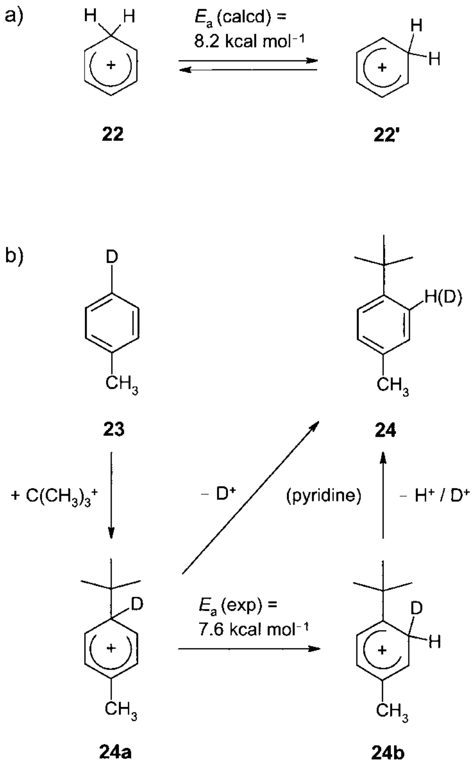
The most convincing proof[25] for the ylide structure of **18** was provided by repeated ion/molecule reactions with D_2O in the flow tube, through which up to five deuterons were incorporated into the anion (**18a**, Scheme 6). In line with the carbanionic structure of **18**, these ions formed covalent adducts with Lewis acids; for example reaction with CO_2 gave the corresponding carboxylate **20** from which the borane fragment could be "evaporated" as a result of the exothermicity of the reaction. This completes the borane-assisted functionalization of **16** in the gas phase to give anion **21**, for example, in analogy to the synthetical sequence (see Scheme 3).



Scheme 6. Characteristic ion/molecule reactions of **18**.

Other methods have also taken advantage of the thermalization of organic ions in the "dense" gas phase to contribute to the wealth of thermodynamic and kinetic data of important organic elementary reactions in recent years. Besides the flowing afterglow techniques, the γ-radiolysis methodology developed by Cacace[29] has been applied by his group[30] to study the chemistry of ions in gas mixtures at pressures of 100–1500 mbar (10^4–1.5×10^5 Pa) and at variable temperature. Carbocations generated under these conditions react by ion/molecule reactions and the ionic products are neutralized subsequently (for example, by deprotonation) to give mixtures of compounds whose composition and structures, respectively, allow one to not only draw mechanistic conclusions but also to derive activation parameters.

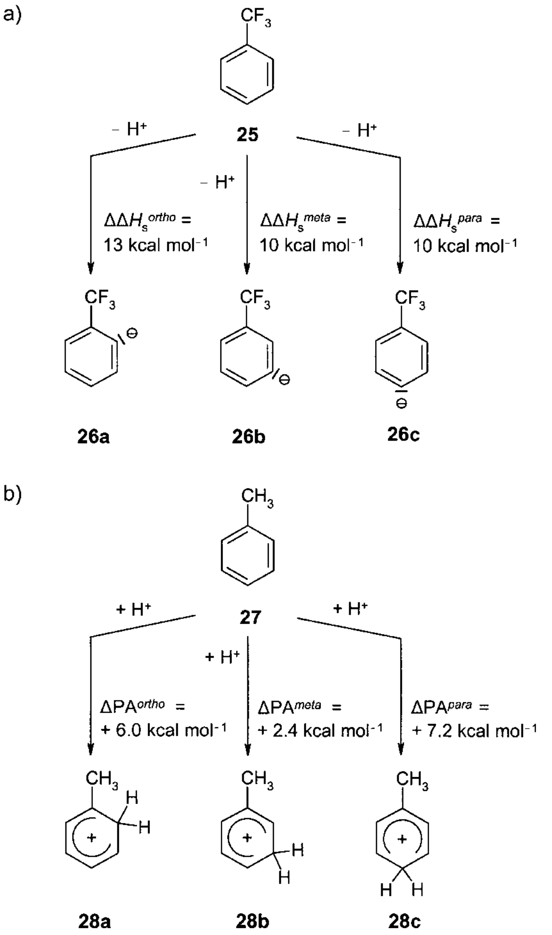
A topic that has been of fundamental interest in physical organic chemistry for half a century addresses the problem of bonding of a proton in a complex with benzene (**22**) and other aromatic nuclei and of its mobility within these resulting complexes (Scheme 7).[31–33] To this end, several studies were performed during recent years in the "dense" gas phase, such as by gas-phase radiolysis[34] and by flowing-afterglow (SIFT) techniques.[35] Thus, the kinetics of deprotonation of radiolytically generated 4-*tert*-butyltoluenium ions **24a** and **24b** yielded the Arrhenius activation energy of the "proton ring walk" in protonated alkylbenzenes (alkylbenzenium ions) (Scheme 7b).[34] This first experimental determination of these gas-phase elementary processes led to a value ($E_a = 7.6 \pm 0.2$ kcal mol^{-1}) that is in excellent agreement with the results of the most recent ab initio calculations ($E_a = 7.9$,[32a] 8.2,[32b] and 7.8 kcal mol^{-1})[32c] and also with the activation energy measured by Olah et al.[36] in 1970 for the proton ring walk in the superacidic liquid phase ($E_a = 10 \pm 1$ kcal mol^{-1}, $\Delta G^{\neq} = 8.0 \pm 1$ kcal mol^{-1});[36c] it represents a landmark in the long research on this ubiquitous isomerization process of arenium ions.



Scheme 7. Proton ring walk a) in benzenium ions and b) in 4-*tert*-butyltoluenium ions **24a** and **24b** generated by ion/molecule reactions in isobutane (ca. 10^5 Pa, 47–120 °C).

Besides the dense gas phase, the "diluted" gas phase continues to represent an important medium for the determination of intrinsic thermodynamic and kinetic data, as demonstrated, for example, by recent investigations on the deprotonation of multiply CF_3-substituted benzenes under the conditions of Fourier transform ion cyclotron resonance (FT-ICR) mass spectrometry.[37] Although FT-ICR mass spectrometers are usually operated under high vacuum, modern instruments offer routine procedures to efficiently cool the ions generated by exothermic ion/molecule reactions. In this case, thermalization is effected by allowing the ions to interact with short-term gas pulses. In a joint effort to compare the deprotonation behavior of trifluoromethylbenzenes towards strong bases in solution[38] and in the gas phase, the groups of Schlosser, Dmowski, and Nibbering[39] found considerable differences between the kinetic and the thermodynamic acidity in solution. The gas-phase studies, however, revealed a notably consistent additivity of the substituent effects. For example, a CF_3 group in the *ortho* position decreases the enthalpy of deprotonation of a C^{arom}–H bond by 13 kcal mol^{-1} and thus the thermodynamic acidity increases almost by a factor of 10^{10}, whereas a CF_3 group in either a *meta* or *para* position to the same C–H bond enhances the acidity by

10 kcal mol^{-1}, that is, by more than a factor of 10^6 (Scheme 8). Additivity of these "local acidities" of trifluoromethylbenzenes in the gas phase are strongly remiscent of the long-known



Scheme 8. a) Increase of the local Brønsted acidities (ΔΔH_s) of trifluoromethylbenzene (**25**) relative to benzene; b) increase of the local proton affinities (ΔPA) of toluene **27** relative to benzene. Note that ΔH_s(Brønsted acid) ≡ PA([(Brønsted acid) – H$^+$]).

additivity of the local proton affinities of methylbenzenes in the gas phase (Scheme 8b).[31, 40] The most recent systematic ab initio calculations on the additivity of substituent effects on the proton affinities of various arenes are in full agreement with these experimental findings.[44]

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"Simple" Carbonyls of Ruthenium: New Avenues from the Hieber Base Reaction

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The rush to develop increasingly more complex and sophisticated transition metal catalysts by ingenious coligand design continues to gather momentum. In this climate it is both refreshing and sobering when results of substantial scientific significance emerge from studies of older and simpler organometallic compounds, which can effectively mediate technologically useful processes. Ultimately, the simpler the system, the more generally applicable are the lessons to be learnt. One such system is provided by the carbonyl chlorides of ruthenium(II), which arise from the carbonylation of alcoholic solutions of commercially available hydrated ruthenium chloride "$RuCl_3 \cdot x\,H_2O$". The resulting yellow solution, described[1a] as including "species of doubtful composition prepared in situ" finds wide use in the preparation of numerous complexes of the form [$RuCl_2(CO)_2L_2$] (L = phosphanes, arsanes, thioethers etc).[1] Not only do such solutions provide access to the carbonyl chemistry of divalent ruthenium. Bruce and Stone first showed that zinc reduction provided the binary zerovalent carbonyl [$Ru_3(CO)_{12}$].[2] This remains the preferred route to this compound, the subsequent chemistry of which has featured in thousands of papers.[3] This early study provided some key insights, including the isolation of dimeric [$Ru_2(\mu\text{-}Cl)_2Cl_2(CO)_6$] (**1**) and the observation that the halide bridges were easily and reversibly cleaved by the weak nucleophile THF to provide *fac*-[$RuCl_2$(thf)$(CO)_3$] (**2**). Chloride also reversibly cleaves dimeric **1**, or replaces the labile THF in **2**, to provide the ruthenate *fac*-[$RuCl_3(CO)_3$]$^-$ (**3**$^-$). In the intervening 33 years, the comparative ignorance of the true nature of the interacting species involved in such alcoholic solutions has been more than excused by the enormous synthetic utility. Recent studies, primarily those of Lavigne and co-workers,[4] have however sought to understand this witches brew, driven in part by the utility of carbonyl halide complexes of divalent ruthenium in various catalytic processes. Amongst these is the water–gas shift

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